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Influence of semi-batch operations on morphological properties of polystyrene made in suspension polymerization

A. L. Nogueira[a], M. B. Quadri[a], P. H. H. Araújo[a], R. A. F. Machado[a] a*

[a]*Federal University of Santa Catarina – UFSC, Chemical Engineering Department, Campus Universitário, Trindade, Caixa Postal 476, Florianópolis – SC, CEP:88040-900, Brazil*

Abstract

Suspension polymerization reactions in industrial processes are usually carried out with batch operations. However, discontinuous systems do not offer process flexibility like semi-continuous ones. Studies and practical applications of semi-batch operations in heterogeneous systems are commonly found for emulsion polymerization systems in order to control copolymer composition, molecular weight, final particle size, particle morphology and reaction rate. On the other hand, semi-batch operations are rarely used to carry out suspension polymerizations. In these systems, this sort of operation strategy can be applied for the production of core-shell particles. The present study intends to show that semi-batch operation can also be used in suspension polymerization systems to manipulate and improve some morphological properties of the produced particles. The styrene suspension polymerization was used as case study. The reactions were carried out considering different monomer feeding rates and reaction times at which the monomer feed stream begins to be added to the system. Results showed that, depending on the semi-batch strategy adopted (*i.e.* reaction time for the beginning of the organic phase feed and feeding rate), it is possible to successfully control some morphological properties of the particles, leading to the production of more uniform particles sizes than those ones obtained in classical suspension systems.

Keywords: Styrene; polystyrene; suspension polymerization process; semi-batch operation

* Corresponding author. Tel.: +55-48-37212431 ; fax: + 55-48-37219687.
E-mail address: ricardo@enq.ufsc.br.

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1. Introduction

Batch processes are frequently used by industries to produce suspension polymers with specific molecular and morphological properties. Despite their limited production capacity, when compared to bulk systems, the use of batch strategies is justified due to the operational facilities and, consequently, the better control of polymer quality parameters. Although their large application, batch operations are considered limited when compared to semi-batch ones.

Nowadays, semi-batch operations are widely used to carry out emulsion polymerizations. In these processes, different semi-batch strategies can be used to control the copolymer composition [1], reaction kinetic [2, 3, 4], molecular weight distribution [5], particle size distribution [6, 7, 8], besides the particle morphology (*i.e.* production of core-shell particles) [9]. Even though the large applications of different semi-batch operation strategies in emulsion polymerizations, the developments and improvements of these processes are restricted to emulsion systems. Therefore, the strategies adopted cannot be directly applied to suspension polymerization processes.

In the last 10 years, a few number of studies had been published regarding the usage of semi-batch strategies in suspension polymerization systems. Most of these works are related to copolymerization systems, and are focused in the control of copolymer composition and/or molecular weight properties [10, 11], besides the production of core-shell particles [12, 13, 14]. Among these studies, those ones that use semi-batch strategies to carry out suspension homopolymerization reactions are scarce [12,15].

A typical suspension polymerization process uses one or more monomers that are insoluble in a continuous phase, usually water. A vigorous stirring process is necessary to disperse the monomer(s) droplets into the continuous phase. One or a cocktail of oil-soluble compounds are frequently used to chemically initiate the polymerization reaction. As the reaction proceeds, the organic phase viscosity increases, constantly changing the breakage and coalescence rate of the monomer-polymer droplets. Due to the increase of the organic phase viscosity, a stabilizing agent must be used to avoid the sticky of the monomer-polymer droplets. The final product of a suspension polymerization reaction is composed by rigid polymer beads (normally spherical) with a characteristic set of morphological properties, *i.e.* mean particle size, particle size distribution, shape and porosity [16].

In suspension polymerizations, a precise control of the particle morphological properties is quite important for storage, transportation, processing and final properties purposes. By manipulation of the stirring frequency, besides the type and concentration of the stabilizing agent, it is possible to adequately manipulate the particle size distribution (PSD) and mean size. Others strategies can be used for the same purpose (*e.g.* perform a bulk pre-polymerization before establishing the suspension or delay the time for the stabilizing agent adding).

The present study intends to show that semi-batch operations can be successfully used to control some morphological properties (*i.e.*, PSD and mean size) of the polystyrene particles produced by suspension polymerization, with practically no effect on the average molecular properties. Two sets of experiments were carried out considering fast and slow kinetics. In each of these sets, distinct feed strategies were employed to evaluate the reactor behavior and their effects on the final polymer properties.

2. Experimental procedures

Semi-batch polymerization reactions were carried out in a 1.0 liter boro-silicate jacketed reactor with an impeller composed by four flat-blades, according to Figure 1. An agitation frequency of 350 RPM was kept constant throughout the reaction. The temperature was controlled and maintained at 90.0°C using a thermostatic bath. Styrene (from *Innova*, 20 ppm of p-terc buthyl catecol) was used as monomer (disperse

phase), dibenzoyl peroxide – BPO (from *Akzo Nobel*) as chemical initiator and poly(vinyl pyrrolidone) – PVP (from *Sul Polímeros*, M_w=360,000 g/mol) as stabilizing agent.

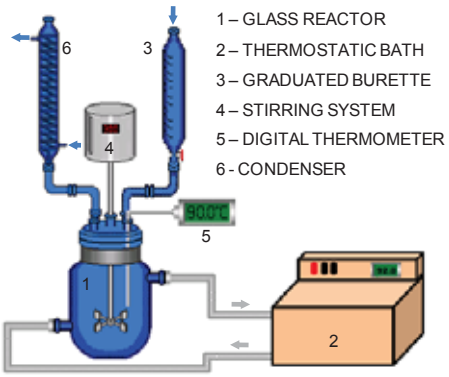

Fig. 1. Schematic representation of the experimental set up

The reactor was initially loaded with approximately 1/3 of the total organic charge, providing a holdup of 0.125. The remaining monomer amount (containing the same initiator concentration) was fed during the reaction up to a holdup of 0.30. A graduated burette was used do feed the organic charge according to the desired volumetric flow. Batch suspension polymerizations were also carried out in the same experimental apparatus to compare the results with those ones obtained using semi-batch strategies.

Two different kinetic conditions were tested: fast (strategies A_1 and A_2: [BPO] = 4.9% wt) and slow (strategies B_1 and B_2: [BPO] = 0.57% wt). Table 1 summarizes the different semi-batch strategies adopted to evaluate the effects of the reaction time at which the organic phase starts to be fed in the system (t_0), and the organic phase feeding flow (t_{feed}), on the particles morphological properties.

Differential granulometric analysis (sieving) and viscosimetry technique were used to estimate the polystyrene PSD and viscosimetric molecular weight, respectively.

Table 1. Batch and semi-batch strategies

Strategy	t_0 (min.)	t_{feed} (min.)	Run
Batch	0.0	0.0	$R1_A$ and $R1_B$
		35.0	R2
Semi-Bacth A_1	5.0	70.0	R3
		105.0	R4
		35.0	R5
Semi-Bacth A_2	100.0	70.0	R6
		105.0	R7
	5.0		R9
Semi-Bacth B_1	70.0	60.0	R10
	150.0		R11
	5.0		R12
Semi-Bacth B_2	70.0	180.0	R13
	150.0		R14

3. Results and discussion

In the first set of experiments (fast kinetic), three different monomer feeding rates were used after 5.0 (A_1) and 100.0 (A_2) minutes of reaction (*i.e.* just after the beginning of the reaction and after the particle identification point – PIP, respectively). Figures 2 and 3 shows the PSD histograms obtained when the reactions were carried out with semi-batch strategies A_1 and A_2, respectively. In each of these figures, the histograms obtained from semi-batch reactions are compared to the histogram obtained from a simple batch reaction ($R1_A$). Besides, a miniature of the histograms plotted as smooth curves are presented in the left up corner of the figures. Table 2 presents the statistical data calculated from PSD histograms showed in Figures 2 and 3 (strategies A_1 and A_2, respectively).

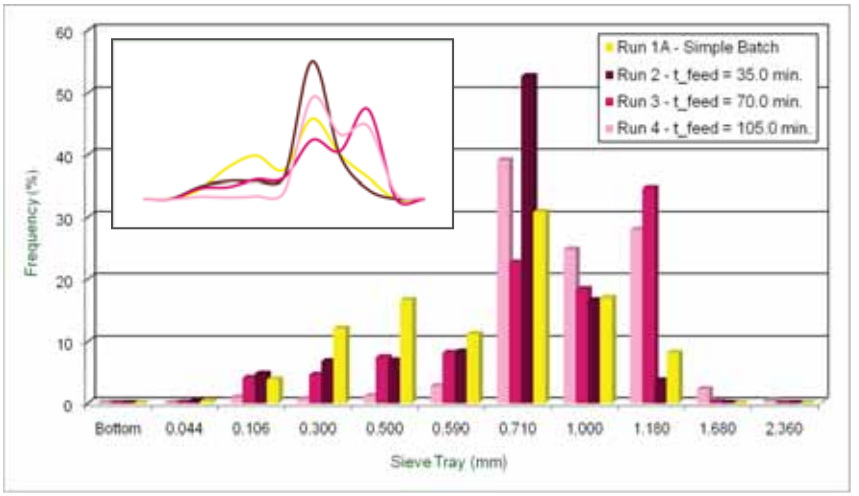

Fig. 2. PSD histograms obtained from semi-batch reactions using strategy A_1 (t_0 = 5.0 minutes).

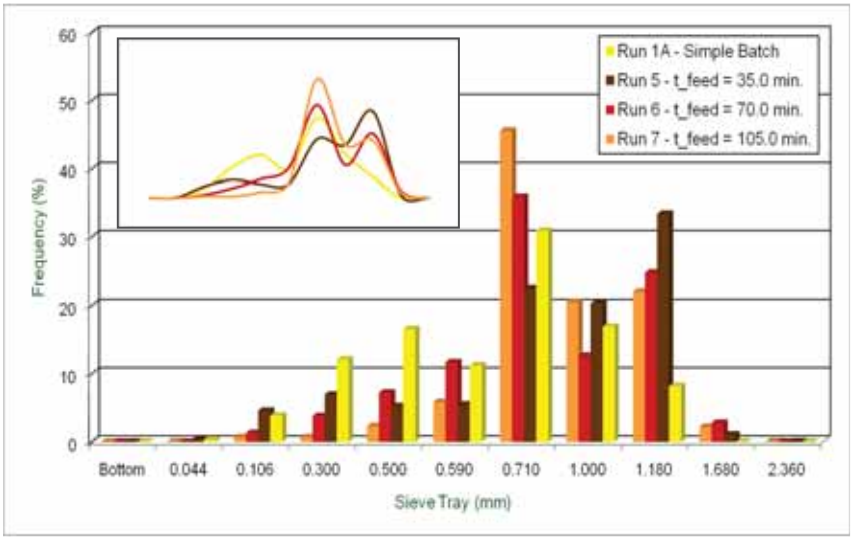

Fig. 3. PSD histograms obtained from semi-batch reactions using strategy A_2 (t_0 = 100.0 minutes)

Table 2. Morphological properties obtained for batch and semi-batch strategies A_1 (t_0 = 5.0 min.) and A_2 (t_0 =100.0 min.)

Run / t_{feed} (minutes)	Size Dispersion	Sauter Mean Diameter (mm)
$R1_A$ / 0.0	0.446	0.869
R2 / 35.0	0.437	0.671
R3 / 70.0	0.549	0.790
R4 / 105.0	0.342	0.978
R5 / 35.0	0.616	0.761
R6 / 70.0	0.474	0.838
R7 / 105.0	0.348	0.929

According to the results presented in Table 2, independent of t_0 (time after de beginning of the reaction to initiate the organic phase feeding), there is an increase of the mean particle diameter and a narrowing of the PSD (excepted for R3) as the feeding rate is reduced (t_{feed} = 35 minutes up to t_{feed} = 105 minutes). These behaviors can be observed in Figures 2 and 3 as a displacement of the histograms toward the larger particles sizes and as a disappearance of the smaller particles sizes as the feeding flow is reduced.

Fast feeding flows (t_{feed} = 35.0 minutes) only narrows the PSD if the organic phase adding starts at the beginning of the reaction (R2 – t_0 = 5.0 minutes). This specific semi-batch strategy is the closer one to the operation condition of the batch reaction. Sufficiently low feeding flows (t_{feed} = 105.0 minutes) leads to a more uniform interaction among new (*low* conversion and viscosity) and old (*high* conversion and viscosity) droplets. It results in a considerable swelling of the existing particles and, consequently, in an increase of the mean particle size and a significant narrowing of the PSD. This behavior can be cleared observed in the histograms of runs 4 and 7 (Figures 2 and 3, respectively), where the smaller size particles practically disappear from the system.

In the second set of experiments (slow kinetics), considering feeding flows with t_{feed} = 60.0 minutes and t_{feed} = 180.0 minutes (strategies B_1 and B_2, respectively), three different reaction times were selected to start the organic phase adding in the system. These specific times represent: beginning of the reaction (t_0 = 5.0 minutes); during gel effect pronunciation (t_0 = 70.0 minutes); after gel effect ending and PIP achievement (t_0 = 150.0 minutes).

Figures 4 and 5 shows the PSD histograms obtained when the reactions were carried out with semi-batch strategies B_1 and B_2, respectively. In each of these figures, the histograms obtained from semi-batch reactions are compared to the histogram obtained from a simple batch reaction ($R1_B$). Besides, a miniature of the histograms plotted as smooth curves is presented in the left up corner of the figures. Table 3 presents the statistical data calculated from PSD histograms showed in Figures 4 and 5 (strategies B_1 and B_2, respectively).

The results obtained for slow kinetic reactions clearly shows that the adopted semi-batch strategies produced larger and less dispersed particles than the ones obtained in the simple batch reaction (Figures 4 and 5, and Table 3). As presented in Table 3, the narrower the PSD (lesser size dispersion) the larger the *Sauter* mean particle size.

For the fast feeding flows experiments (t_{feed} = 60.0 minutes), the narrower PSD were obtained when the organic phase started to be added into the system during the gel effect pronunciation (*i.e.* t_0 = 70.0 minutes). For the slow feeding flows experiments (t_{feed} = 180.0 minutes), it was just possible to produce less dispersed particles when the organic phase started to be fed into the system in the beginning of the reaction (t_0 = 5.0 minutes). These results suggest that the production of polystyrene beads with the narrower PSD depends on a combination of the moment to initiate the organic phase adding and the feeding flow. In other words, there should be a specific and limiting moment to initiate the organic phase feeding, which is directly related to the viscosity of the dispersed phase, to produce the narrower PSD. After this specific time, more dispersed particles should be produced.

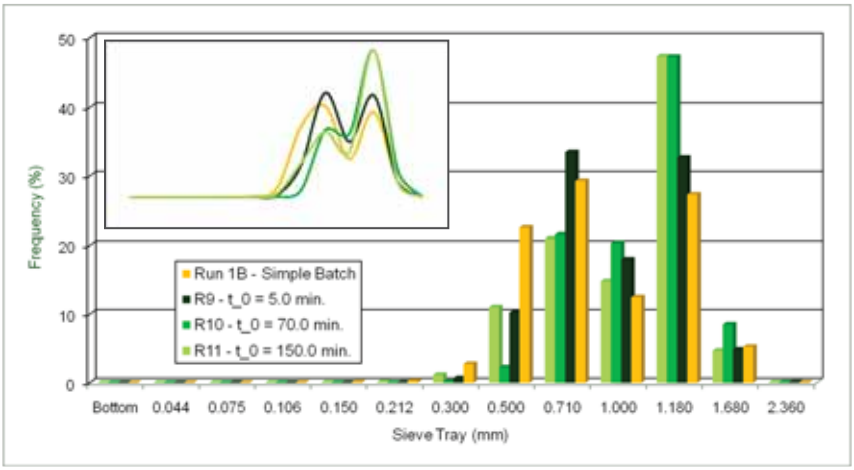

Fig. 4. PSD histograms obtained from semi-batch reactions using strategy B_1 (t_{feed} = 60.0 minutes)

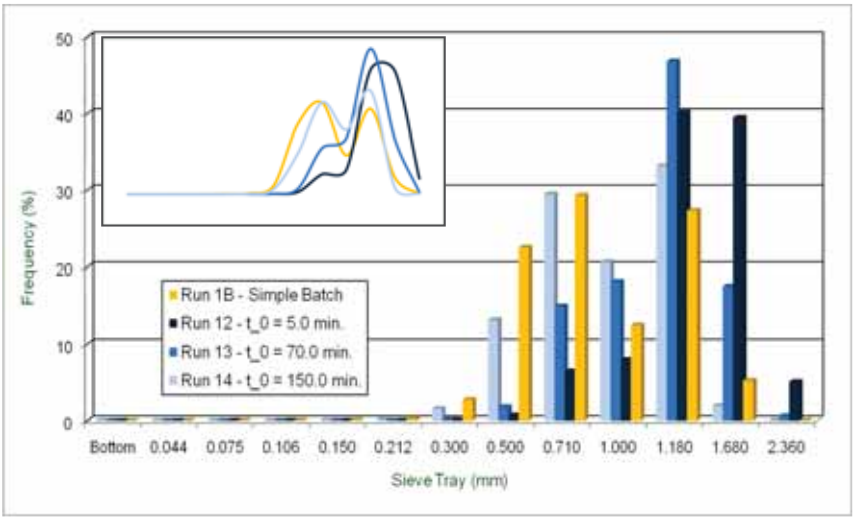

Fig. 5. PSD histograms obtained from semi-batch reactions using strategy B_2 (t_{feed} = 180.0 minutes)

Table 3. Morphological properties obtained for batch and semi-batch strategies B_1 (t_{feed} = 60.0 min.) and B_2 (t_{feed} = 180.0 min.)

Run / t_{feed} (minutes)	Size Dispersion	Sauter Mean Diameter (mm)
$R1_B$ / 0.0	0.481	0.884
R9 / 5.0	0.373	1.002
R10 / 70.0	0.301	1.174
R11 / 150.0	0.366	1.051
R12 / 5.0	0.291	1.509
R13 / 70.0	0.317	1.262
R14 / 150.0	0.364	0.965

This behavior might be a consequence of diffusion problems of the new monomer-initiator droplets toward in the monomer-polymer droplets already existing in the system. In other words, the viscosity of the existing monomer-polymer droplets should be sufficient high to inhibit the diffusion of the fresh monomer added into the system, leading to the formation of new particles. As a consequence, it was observed a reduction of the *Sauter* mean diameter and an increase of the particles size dispersion with the delaying of the moment to initiate the organic phase adding (Table 3).

According to the results, the later the moment to initiate de organic phase adding, the faster should be the organic phase feeding flow to produce more homogeneous particles (narrow PSD). For slow feeding flows, the later the moment to initiate de organic phase feeding, the wider the PSD and the smaller the produced particles. Hence, depending on the selected value of t_0 and t_{feed}, diffusion problems may occur in the system, leading to the formation of new and smaller particles rather than the coating or swelling of the existing ones by the organic phase recently fed into the system. This behavior can be clearly observed in Figure 5, where it is possible to notice the growing of a shoulder in the PSD between 0.5 and 1.0 mm as t_0 increase from 5.0 up to 150 minutes. In Figure 4, this behavior can also be verified (subtle appearance of particles with 0.5 mm), but not so clearly than in Figure 5 due to the "high" feeding flow adopted, which leads to a more pronounced solubilization of the existing monomer-polymer droplets.

The average molecular weights were determined using the viscosimetry technique, as mentioned in section 2. The obtained results showed that semi-batch operations did not affect significantly the viscosimetric polymer molecular weight in the fast and slow kinetic experiments. In the first case (fast kinetic), considering the products obtained in the reactions $R1_A$, R2, R3, R4, R5, R6 and R7, an average viscosimetric molecular weight of 30,000 ± 4,000 g/mol was obtained. In the second case (slow kinetic), considering the products obtained in the reactions $R1_B$, R9, R10, R11, R12, R13 and R14, an average viscosimetric molecular weight of 150,000 ± 10,000 g/mol was obtained. According to the gravimetric analyses, the monomer conversion was greater than 96% for all the reactions.

4. Conclusions

According to the results, the styrene suspension polymerization can be carried out in a semi-batch way to successfully produce polystyrene beads with a narrower PSD then the one obtained using classic batch operations. Although the increase in the particles sizes, a simple recipe correction (*e.g.* stabilizing agent concentration) can be realized to minimize this effect due to the employing of a semi-batch strategy.

The observed behavior suggest that the interaction among new (*low* conversion and viscosity) and old (*high* conversion and viscosity) droplets is governed by a diffusion process, which is directly dependent of the reaction kinetics (*i.e.* molecular weight) and viscosity of the dispersed phase already existing in the system (*i.e.* reaction time).

Therefore the viscosity of the dispersed phase, which also depends on the polymer molecular weight, seems to be the most important factor to be taken in to account when a semi-batch strategy is applied. Depending on the reaction kinetics and the moment of the reaction (time after the reaction beginning), the organic phase feeding flow should be carefully adjusted to avoid diffusion problems and, consequently, produce particles with narrow PSD.

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